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(54) Title: DURABLE AND REGENERABLE MICROBIOCIDAL TEXTILES

(57) Abstract

The present invention provides, *inter alia*, durable and regenerable microbiocidal textiles and methods for preparing such textiles. Such textiles can be readily prepared using a wet finishing process to covalently attach a heterocyclic *N*- halamine to a cellulose based material or other polymeric material. Once prepared, the textiles of the present invention have a broad spectrum of biocidal activity against pathogenic microorganisms. Moreover, the biocidal activity of such textiles can be regenerated by washing with a halogenated solution.

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DURABLE AND REGENERABLE MICROBIOCIDAL TEXTILES

BACKGROUND OF THE INVENTION

An important and growing part of the textile industry is the medical and related healthcare and hygiene sectors. Textile materials used in medical-related applications include, for example, surgeon's gowns, caps and masks, patient drapes, bandages, wipers and cover cloths of various sizes. Such textile materials, however, are conductive to cross-infection and transmission of diseases caused by microorganisms. As such, the possibility of spreading infections caused by the lethal HIV virus, the insidious hepatitis virus or other epidemic diseases has created an increased concern regarding the use of protective facilities and uniforms for workers in the medical/healthcare/hygiene sectors. Currently, textile materials used in medical applications are disposable, nonwoven synthetic fabrics which are neither biocidal nor reusable. Such textile fabrics provide protection by blocking the transmission of microorganisms, rather than by inhibiting the growth of the microorganisms. Thus, cross-infection through surface contact of the contaminated textile fabrics is problematic. As a result, in an effort to prevent the cross-infection and transmission of diseases, the contaminated materials must be appropriately sterilized and discarded after use. Unfortunately, such sterilization and discarding procedures result in substantial increases in the cost of healthcare and in the amount of bio-hazardous wastes that are generated.

Accordingly, it is desirable that bacterial infections resulting from contact with contaminated textiles be reduced or eliminated, and that transmission of pathogenic bacteria from person to person during wear or use of contaminated textiles be prevented by inhibiting the growth of the microorganisms on fabrics. Moreover, it is desirable that surgeon's dresses, hospital carpeting and bedding materials, underwear, socks, and uniforms be biocidal so as to provide the best protection possible. In addition, it is desirable to have biocidal textiles for use in, *inter alia*, hotel-use towels, bedding materials, socks and other hygienic products as well.

Currently, there are two general categories of technologies which can provide protection for medical/healthcare/hygiene personnel. They are (1) physical techniques which involve the formation of a physical barrier against microbial infiltration or transmission by selecting fabric constructions and coatings that are impermeable or that are microporous and contain antimicrobial agents; and (2) chemical technologies which involve the incorporation of active functional agents onto fabrics or fibers by grafting or other chemical methods. Disposable materials are examples of the first category. The coating methods involve the application of impermeable materials onto the surface of fabrics, thereby blocking the infiltration and permeation of microorganisms. However, cross-infection and spreading of diseases through the contact of the coating surface is still feasible and, thus, pose potential threats to workers who handle the contaminated materials. Moreover, the impermeable properties can cause wearers to become uncomfortable and, in turn, to become less efficient.

As such, the chemical association of antibacterial agents onto either the surface or entirety of the material appears to be more practical in terms of durability and efficacy of the antibacterial properties. There are two major pathways to chemically achieve durable antibacterial effects. In one pathway, the slow-releasing of biocides through contact with the processed fabrics is employed. In this pathway, a pathway widely used around the world, sufficient chemical agents are impregnated onto the fibers by either chemical or physical methods. Thereafter, the biocides are slowly released from the processed fabrics into the media, thereby contacting and inhibiting the growth of microorganisms. Unfortunately, such chemical agents can be washed away easily if they are not covalently impregnated onto the surface of the fabrics. Moreover, the antibacterial functions are non-regenerable.

In the second pathway, a more innovative technology is employed which involves chemical modification of textile materials with biocidal or potential biocidal compounds, wherein the antibacterial properties of such compounds are regenerable with a simple washing. The potential antibacterial groups can be rendered biocidal after washing with certain common chemicals, such as diluted bleaching solutions. Over thirty-five years ago, Gagliardi, *et al.* first proposed the regeneration principle of antibacterial finishing, hoping to regenerate the lost function by washing the used fabrics with some specific solutions (*see*, *Am. Dyest. Reptr.*, 51, 49 (1962). However, although much effort has been expended, no commercial products have resulted.

In view of the foregoing, there exists a need in the art for durable and regenerable microbiocidal textiles. The present invention remedies such need by providing, *inter alia*, durable and regenerable microbiocidal textiles.

SUMMARY OF THE INVENTION

The present invention provides, *inter alia*, durable and regenerable microbiocidal textiles and methods for preparing same. Such textiles can be readily prepared using a classical wet finishing process to covalently attach a heterocyclic *N*-halamine to a cellulose based material or other polymeric material. Once prepared, the textiles of the present invention have a broad spectrum of biocidal activity against pathogenic microorganisms. Moreover, the biocidal activity of such textiles can be regenerated by washing with a halogenated solution.

In one embodiment, the present invention provides a process for preparing a microbiocidal cellulosic, cellulosic/polyester or polyester textile precursor, the process comprising: (a) immersing a cellulosic, cellulosic/polyester or polyester textile in an aqueous treating solution which comprises a heterocyclic *N*-halamine, a wetting agent and a catalyst; (b) removing the excess treating solution from the cellulosic, cellulosic/polyester or polyester textile; (c) drying the cellulosic, cellulosic/polyester or polyester textile; (d) curing the dried cellulosic, cellulosic/polyester or polyester textile; (e) washing the cured cellulosic, cellulosic/polyester or polyester textile to remove excess reagents; and (f) drying the treated cellulosic, cellulosic/polyester or polyester textile to remove water.

In another embodiment, the present invention provides a process for rendering a cellulosic, cellulosic/polyester or polyester textile microbiocidal, the process comprising: (a) washing a microbiocidal cellulosic, cellulosic/polyester or polyester textile precursor with a halogenated solution, the microbiocidal textile precursor being prepared in accordance with the above method; and (b) drying the treated microbiocidal cellulosic, cellulosic/polyester or polyester textile to remove water. In the process, the halogenated solution can be a chlorine solution or, alternatively, a bromine solution. In a presently preferred embodiment, the halogenated solution is a chlorine solution (*e.g.*, a chlorine bleach solution such as Clorox). The washing of the microbiocidal cellulosic, cellulosic/polyester or polyester textile precursor with a halogenated solution renders the textile biocidal and, in addition, it sterilizes the textile.

In yet another embodiment, the present invention provides a composition for finishing fabrics, *i.e.*, an aqueous treating solution, the composition comprising a wetting agent; and a heterocyclic *N*-halamine. In a preferred embodiment, the composition further includes a catalyst. In an even more preferred embodiment, the composition further includes additives (*e.g.*, softeners and waterproofing agents) to impart favorable characteristics to the composition.

There are a myriad of application areas for the microbiocidal textiles of the present invention. For instance, the microbiocidal textile materials can provide biocidal protective clothing to personnel in the medical area as well as in the related healthcare and hygiene areas. In contrast to previously used textiles, the textiles of the present invention are not a barrier to microorganisms, but rather a disinfectant to them. As such, the regenerable and reusable biocidal materials can replace currently used disposable, nonwoven fabrics as medical textiles, thereby significantly reducing hospital maintenance costs and disposal fees. The microbiocidal properties of the textiles of the present invention can be advantageously used for women's wear, underwear, socks, and for other hygienic purposes. In addition, the microbiocidal properties can be imparted to carpeting materials to create odor-free and germ-free carpets. Moreover, all germ-free environments, such as required in biotechnology and pharmaceutical industry, would benefit from the use of the microbiocidal textiles of the present invention to prevent any contamination from air, liquid and solid media.

Other features, objects and advantages of the invention and its preferred embodiments will become apparent from the detailed description which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates examples of heterocyclic *N*-halamines which are suitable for use in the present invention.

FIG. 2 illustrates an exemplar reaction scheme whereby the heterocyclic *N*-halamine is covalently attached to cellulose.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

In one embodiment, the present invention provides a process for preparing a microbiocidal cellulosic, cellulosic/polyester or polyester textile precursor, the process comprising: (a) immersing a cellulosic, cellulosic/polyester or polyester textile in an aqueous treating solution which comprises a heterocyclic *N*-halamine, a wetting agent and a catalyst; (b) removing the excess treating solution from the cellulosic, cellulosic/polyester or polyester textile; (c) drying the cellulosic, cellulosic/polyester or polyester textile; (d) curing the dried cellulosic, cellulosic/polyester or polyester textile; (e) washing the cured cellulosic, cellulosic/polyester or polyester textile to remove excess reagents; and (f) drying the treated cellulosic, cellulosic/polyester or polyester textile to remove water.

"Heterocyclic *N*-halamine," as used herein, refers to a 4- to 7-membered ring, wherein at least 3 members of the ring are carbon, and from 1 to 3 members of the ring are nitrogen heteroatom, and from 0 to 1 member of the ring is oxygen heteroatom, wherein from 0 to 2 carbon members comprise a carbonyl group, and wherein at least 1 to 3 nitrogen atoms are substituted with a hydroxyalkyl group, such as —CH_2OH, or a alkoxyalkyl group, such as -CH_2OCH_3. In addition, the ring members can be further substituted with alkyl groups, such as methyl, ethyl, *etc.* Heterocyclic *N*-halamines are generally disclosed in U.S. Patent No. 5,490,983 issued to Worley, *et al.* on February 13, 1996, the teachings of which are incorporated herein by reference for all purposes.

Heterocyclic *N*-halamines suitable for use in accordance with the present invention include, but are not limited to, the following: monomethylol-5,5-dimethylhydantoin (MDMH), 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH); monomethylolated and dimethylolated derivatives of 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid and 5,5-dimethylhydantoin; and monomethoxylated and dimethoxylated derivatives of 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid and 5,5-dimethylhydantoin. Examples of the monomethoxylated and dimethoxylated compounds are monomethoxymethyl-5,5-dimethylhydantoin and 1,3-dimethoxymethyl-5,5-dimethylhydantoin, respectively. In a presently preferred embodiment, monomethylol-

5,5-dimethylhydantoin and 1,3-dimethylol-5,5-dimethylhydantoin are the heterocyclic *N*-halamines employed.

The heterocyclic *N*-halamines used in the present invention are commercially available from a number of different sources. For instance, monomethylol-5,5-dimethylhydantoin (MDMH) and 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH) are commercially available under the tradenames DANTOIN® and GLYDANT® XL-1000, respectively, from LONZA, INC. (Fair Lawn, NJ). Moreover, cyanuric acid is commercially available from ALDRICH® (Milwaukee, WI). In addition, those of skill in the art will readily appreciate that the heterocyclic *N*-halamines used in the present invention can be synthesized in a variety of ways using conventional synthetic chemistry techniques. In this connection, those of skill will readily appreciate that the dimethoxylated derivatives are prepared from the dimethylated derivatives, whereas the monomethoxylated derivatives are prepared from either the mono- or dimethylated derivatives.

Examples of heterocyclic *N*-halamines suitable for use in the present invention are set forth in FIG. 1. It should be noted that many of these heterocyclic *N*-halamines are widely used in cosmetic products and their halogenated derivatives are major disinfectants for use in, for example, swimming pools. As such, these compounds will not generate any toxic effects for humans or for the environment either in terms of the finished fabric or during the finishing process.

"Microbiocidal," as used herein, refers to the ability to kill at least some types of microorganisms, or to inhibit the growth or reproduction of at least some types of microorganisms. The textiles prepared in accordance with the present invention have microbiocidal activity against a broad spectrum of pathogenic microorganisms. For example, such textiles have microbiocidal activity against representative gram-positive (such as *Staphylococcu aureus*) and gram-negative bacteria (such as *Escherichia coli*). Moreover, quite importantly, the microbiocidal activity of such textiles is readily regenerable.

In step (a) of the above process, the aqueous treating solution (or, alternatively, finishing solution or bath) comprises a heterocyclic *N*-halamine as described above, a wetting agent and a catalyst. As used herein, "wetting agent" refers to a substance that increases the rate at which a liquid spreads across a surface, *i.e.*, it renders a surface nonrepellent to a liquid. Examples of suitable wetting agents include,

but are not limited to, Triton X-100 (Sigma Chemical Co., St. Louis, MO), SEQUAWET® (Sequa Chemical Inc., Chester, SC), and AMWET® (American Emulsions Co., Dalton, GA). Other wetting agents suitable for use in the present invention will be known to and used by those of skill in the art. As used herein, "catalyst" refers to a substance which augments the rate of a chemical reaction without itself being consumed. Suitable catalysts for use in the present invention include, but are not limited to, the following: magnesium salts, zinc salts and ammonium salts. In a presently preferred embodiments, the catalyst employed is one of the following: $MgCl_2$, $Mg(NO_3)_2$, $Zn(NO_3)_2$ or NH_4NO_3.

Those of skill in the art will readily appreciate that the concentration of the various components of the aqueous treating solution can be widely varied depending upon the particular components employed and the results desired. Typically, the heterocyclic *N*-halamine is present at a concentration of at least about 0.2%. More typically, the heterocyclic *N*-halamine is present at a concentration ranging from about 0.2% to about 20%, more preferably at a concentration ranging from about 0.5% to about 10% and, more preferably, at a concentration ranging from about 1% to about 5%. It will be readily apparent to those of skill in the art that higher heterocyclic *N*-halamine concentrations (*e.g.*, 50%) can be employed, but such higher concentrations are not required to impart microbiocidal activity. Again, suitable microbiocidal activity can be imparted using a heterocyclic *N*-halamine concentration as low as about 0.2%. The wetting agent is typically present at a concentration ranging from about 0.1% to about 3% and, more preferably, at a concentration ranging from about 0.2% to about 1%. The concentration of the catalyst employed will depend on the concentration of the heterocyclic *N*-halamine employed. Typically, the ratio of heterocyclic *N*-halamine to catalyst present will range from about 10:1 to about 5:1. The pH of the aqueous treating solution will typically range from a pH of about 2 to about 6 and, more preferably, from a pH of about 2.5 to about 4.5.

Those of skill in the art will readily appreciate that other additives can be incorporated into the aqueous treating solution to impart favorable characteristics to the cellulosic, cellulosic/polyester or polyester textile. Such additives can include softeners and waterproofing agents which are known to and used by those of skill in the art. Examples of softeners which can be added to the aqueous treating solution include, but are not limited to, MYKON and SEQUASOFT®, both of which are commercially

available from Sequa Chemical Inc. (Chester, SC). Examples of waterproofing agents which can be added to the aqueous treating solution include, but are not limited to, SEQUAPEL® (Sequa Chemical Inc., Chester, SC), SCOTCHGARD (3M, St. Paul, MN) and other water repellent finishing solutions used by those of skill in the art.

In carrying out step (a), the textile used may be roving, yarn or fabric regardless of whether spun, knit, or woven, or may be nonwoven sheets or webs. Moreover, the textile may be made of cellulosic fibers, polyester fibers or blends of these fibers. In addition, other polymer materials having reactive functional groups (*e.g.*, —OH groups) can be used. Such polymer materials include, but are not limited to, polyvinyl alcohol (PVA), starches and proteins. In wetting the textile in the finishing or treating bath, ordinary textile equipment and methods suitable for batchwise or continuous passage of roving, yarns or fabrics through an aqueous solution may be used, at any speed permitting thorough and uniform wetting of the textile material.

In step (b), the excess aqueous treating solution is removed by ordinary mechanical methods such as by passing the textile between squeeze rolls, by centrifugation, by draining or by padding. In a preferred embodiment, the excess aqueous treating solution is removed by padding.

In step (c), the cellulosic, cellulosic/polyester or polyester textile is dried at a temperature ranging from about 50°C to about 90°C and, more preferably, at a temperature ranging from about 75°C to about 85°C for a period of time ranging from about 3 to about 8 minutes and, more preferably, for about 5 minutes.

In step (d), the dried cellulosic, cellulosic/polyester or polyester textile is cured at a temperature ranging from about 120°C to about 180°C and, more preferably, at a temperature ranging from about 140°C to about 160°C for a period of time ranging from about 3 to about 8 minutes and, more preferably, for about 5 minutes. The heating can be carried out in an oven, preferably one having a forced draft of air directed at the surface of the textile and exhausting through a vent to remove fumes.

In step (e), the dried cellulosic, cellulosic/polyester or polyester textile is washed. Washing of the treated textile, *i.e.*, *step (e)*, can be done with either hot or cold water. The covalent bonds formed are stable, insoluble, and durable to the mechanical agitation, spraying and rubbing that occurs in washing machines or in large scale continuous or batchwise textile washing equipment.

Final drying, *i.e.*, *step (f)*, can be carried out by any ordinary means such as oven drying, line drying or tumble drying in a mechanical clothes dryer. A drying temperature of about 80° to about 120°C for less than 15 minutes is particularly preferred.

In another embodiment, the present invention provides a process for rendering a cellulosic, cellulosic/polyester or polyester textile microbiocidal, the process comprising: (a) washing a microbiocidal cellulosic, cellulosic/polyester or polyester textile precursor with a halogenated solution, the microbiocidal textile precursor being prepared in accordance with the above method; and (b) drying the treated microbiocidal cellulosic, cellulosic/polyester or polyester textile to remove water. In the process, the halogenated solution can be a chlorine solution or, alternatively, a bromine solution. In a presently preferred embodiment, the halogenated solution is a chlorine solution (*e.g.*, a chlorine bleach solution such as Clorox). The washing of the microbiocidal cellulosic, cellulosic/polyester or polyester textile precursor with a halogenated solution renders the textile biocidal and, in addition, it sterilizes the textile. Moreover, as previously explained, the microbiocidal activity, *i.e.*, oxidative properties, of the textiles can be regenerated by periodically washing the textile with a halogenated solution during regular washings.

In yet another embodiment, the present invention provides a composition for finishing fabrics, the composition comprising a wetting agent; and a heterocyclic *N*-halamine. In a preferred embodiment, the composition further includes a catalysts. In an even more preferred embodiment, the composition further includes additives (*e.g.*, softeners and waterproofing agents) to impart favorable characteristics. The discussions pertaining to the heterocyclic *N*-halamines, wetting agents, catalysts, additives and their various concentrations are fully applicable to this composition and, thus, such discussions will not be repeated again. The pH of the aqueous treating solution will typically range from a pH of about 2 to about 6 and, more preferably, from a pH of about 2.5 to about 4.5. Those of skill in the art will readily appreciate that the above composition can be prepared in a concentrated form or, alternatively, in a form suitable for immediate use, *i.e.*, at appropriate reagent concentrations.

Considering both antibacterial and mechanical properties of the finished textiles prepared using the methods and compositions set forth herein, those of skill will readily appreciate that such finished textiles can advantageously be used in the

preparation of the following articles: surgeon's gowns, caps, masks, surgical covers, patient drapes, carpeting, bedding materials, underwear, socks, uniforms, *etc.* Those of skill in the art will readily appreciate that the finished textiles of the present invention can also advantageously be used for a variety of other purposes, such as in hotel-use towels, bedding materials, hygienic products, in various clothing to protect against pesticides and other toxic chemicals, *etc.*

The invention will be described in greater detail by way of specific examples. The following examples are offered for illustrative purposes, and are intended neither to limit or define the invention in any manner.

EXAMPLES

Example 1

This example illustrates the finishing of fabrics with monomethylol-5,5-dimethythydantoin (MDMH or Anti-1).

A finishing bath containing 24 grams of monomethylol-5,5-dimethyl-hydantoin, 4.8 grams magnesium chloride, and 0.6 gram of Triton X-100 (a wetting agent) in 600 milliliters of deionized water was prepared. The pH of the finishing bath was adjusted to 3.4 with one milliliter of 0.1 N HCl solution. Then, 140.9 grams of pure cotton fabric (#400 Testfabrics, Inc., Middlesex, NJ) and 141.4 grams of cotton/polyester (35/65) blend fabric (#7409, Testfabrics, Inc., Middlesex, NJ) were dipped in the bath for more than five minutes and padded through a padder with a more than 80% pick-up rate. The fabrics were dipped and padded again, and dried at 80° C for 5 minutes. The fabrics were then cured at 160° C for 5 minutes. Finally, the finished fabrics were machine washed with 90 grams of American Association of Textile Chemists and Colorists (AATCC) Standard Reference Detergent 124 at a low water level and a temperature of about 60° C for 30 minutes. The fabrics were dried and weighed, yielding 42.8 grams (1.35% add-on) of the cotton fabric and 142.4 grams (0.71% add-on) of the cotton/polyester blend fabric. The cotton product exhibited prominent infrared adsorption bands in a KBr pellet at 1718 and 1770 cm^{-1}.

Thereafter, the finished fabrics were washed with a diluted Clorox solution containing about 0.01% active chlorine. Antibacterial properties of the fabrics were tested against representative gram-positive bacteria (such as *Staphylococcu aureus* (ATCC

5368)) and gram-negatibe bacteria (such as *Escherichia coli* (ATCC 2666)) using the protocol set forth in Example III.

Example II

This example illustrates the finishing of fabrics with 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH or Anti-2).

A finishing bath containing 48 grams of 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH or Anti-2), 9.6 grams magnesium chloride and 0.8 gram of Triton X-100 (a wetting agent) in 800 milliliters of deionized water was prepared. The pH of the finishing bath was adjusted to 3.1 with 20 milliliters of 0.01 N HCl solution. Then, 144.7 grams of pure cotton fabric (#400 Testfabrics, Inc., Middlesex, NJ) and 143.2 grams of cotton/polyester (35/65) blend fabric (#7409, Testfabrics, Inc., Middlesex, NJ) were dipped in the bath for more than five minutes and padded through a padder with more than an 80% pick up rate. The fabrics were dipped and padded again, and dried at 80° C for 5 minutes. The fabrics were then cured at 160° C for 5 minutes. Finally, the finished fabrics were machine washed with 90 grams of AATCC Standard Reference Detergent 124 at a low water level low and a temperature of about 60° C for 30 minutes. The fabrics were dried and weighed, yielding 147.9 grams (2.22% add-on) of the cotton fabric and 145.5 grams (1.62% add-on) of the cotton/polyester blend fabric. The cotton product exhibited prominent infrared adsorption bands in a KBr pellet at 1718 and 1770 cm^{-1}.

Thereafter, the finished fabrics were washed with a diluted Clorox solution containing about 0.01% active chlorine. Antibacterial properties of the fabrics were tested against representative gram-positive bacteria (such as *Staphylococcu aureus* (ATCC 5368)) and gram-negatibe bacteria (such as *Escherichia coli* (ATCC 2666)) using the protocol set forth in Example III.

Example III

This example illustrates the qualitative antibacterial study of the Anti-1 finished fabrics carried out using the AATCC Test Method 147.

Fabric samples of #405 (pure cotton, Testfabrics, Inc., Middlesex, NJ) and # 7402 (cotton/polyester 35/65, Testfabrics, Inc., Middlesex, NJ) were finished in a manner similar to that set forth in Example I. The concentration of the finishing agent used was from about 5 to 15% in the finishing of the cotton fabrics and from about 5 to 20% in the finishing of the cotton/polyester (35/65) blend fabric because of the lower concentration of cellulose in the blend. The final biocidal property was imparted onto the finished fabrics by washing them with a diluted Clorox solution containing 0.25% chlorine after each washing cycle. Qualitative antibacterial tests were conducted according to AATCC Test Method 147.

In the AATCC Test Method 147, two pieces of chlorinated fabric having the size of 25 mm X 50 mm were placed on a nutrient agar plate which had been inoculated by five streaks of a diluted bacteria solution using a 4 mm inoculating loop. The diluted bacteria solution was prepared by transferring 1.0 milliliter of 24 hour broth culture into 9.0 milliliter of sterile distilled water. The agar plate was incubated at 37° C for 18-24 hours. The minimum width of inhibition zone along a streak on either side of the test specimen are measured. Table I sets forth the qualitative biocidal evaluations of the finished fabrics with different concentration of the agent Anti-1. Even with a 5% finishing agent concentration and about a 1% add-on of the agents, the processed fabrics exhibit durable and regenerable antibacterial properties.

Table I. Results of Finished Cotton (#405) and Cotton/Polyester 35/65 (#7402)

Fabric	Conc. of Anti-1 (%)	Add-on %	Biocidal Results* After 20 Times Washing *E.coli*	*S.aureus*	Biocidal Results After 50 Times Washing *E.coli*	*S.aureus*
#405	5	1.2	>3 mm	>1 mm	>1 mm	~1 mm
	10	2.3	>8 mm	>3 mm	>3 mm	>1 mm
	15	3.1	kill all	kill all	>4 mm	>4 mm
#7402	5	0.8	>3 mm	>1 mm	>1 mm	~1 mm
	10	1.4	>3 mm	>1 mm	>2 mm	~1 mm
	15	1.6	kill all	kill all	>2 mm	>1 mm
	20	2.0	kill all	>4 mm	>3 mm	>1 mm

* Biocidal results were tested with AATCC test method 147, the minimum disinfection distance is measured in millimeter (mm). Washing tests were conducted with machine wash warm according to AATCC test method 124 and AATCC Standard Reference Detergent 124 was used.

Example IV

Four types of clothing materials, *i.e.*, #400, #7402 (35/65 cotton/polyester), Terry cloth and Rayon (all from Testfabrics, Inc., Middlesex, NJ), were chemically finished with the functional agent following the protocol set forth in Example I. The antibacterial results of the different fabrics finished with Anti-1 are shown in Table II. The percentage of add-on of functional agents by the fabrics was only about 1%. However, after activation of the biocidal properties of the fabrics by washing the fabrics with diluted Clorox, the zones of inhabitation of bacteria were relatively large. The results indicate that the cellulose-containing materials can easily incorporate with the functional finishing agents and obtain the desired function against microorganisms in a broad spectrum. If complete disinfection is required, the add-on rate of the finishing agents can be increased by increasing the concentration of the agents as discussed above. However, in most applications, only appropriate biocidal properties are needed, especially in the anti-odor finishes.

Table II. Antibacterial Results of Different Fabrics Finished with Anti-1

Fabrics	% Add-on of the agent	Biocidal results against *S.aureus* after being activated (mm)	Biocidal results against *E.coli* after being activated (mm)
Cotton cloth #400	1.43	> 1.0	> 2.0
Rayon	1.21	> 1.0	> 1.0
Dacron/Cotton 65/35 #7402	1.19	> 4.0	> 10
Terry cloth 100% Cotton	1.40	kill all	> 10
Control Cotton cloth #400	/	all grow	all grow

Example V

This example illustrates the quantitative antibacterial study (AATCC Test Method 100) of Anti-1 finished fabrics.

Quantitative studies of biocidal properties of the Anti-1 finished fabrics indicates that even at a very low concentration of the finishing bath, biocidal properties on fabrics can be obtained. AATCC Test Method 100 was adopted in this study. According to this test method, four pieces of staked circular fabric swatches 4.8 ± 0.1 (about one grams) were inoculated with 1.0 ± 0.1 milliliter of inoculum in a 250 milliliter jar. The inoculum was a nutrient broth culture containing over 1.0×10^6 clone forming units (CFU) of organisms. After the swatches were inoculated, they were neutralized by 100 milliliter of a 0.02% sodium thiosulfate solution in the jar. The contact time was the time between inoculation and neutralization. The jar was vigorously shaken and the neutralized solution was diluted in serial. The dilutions, usually 10^0, 10^1, and 10^2, were plated on nutrient agar and incubated for 18-24 hours at 37° C. The number of bacteria recovered from the inoculated finished fabrics was counted and compared with that from untreated fabrics. Six log reduction means the total inactivation of bacteria, and one log reduction means that finished fabrics reduced bacteria counts from 10^6 CFU to 10^5 CFU. Finished fabrics prepared from solutions containing 1%-6% of monomethylol-5,5-dimethylhydantoin following the protocol set forth in Example I

with pickup rates below 1% have been tested. The biocidal properties of such fabrics are set forth in Table III.

Table III. Effects of Finishing Concentrations of Anti-1 on Bacterial Reduction Rates.

Conc. of agent Anti-1	Material	Take up %	Bacterial reduction rates on contact time					
			0 min		30 min		60 min	
			E. coli	S. aureus	E. coli	S. aureus	E. coli	S. aureus
1%	#400	0.65	No	No	No	1 log	No	No
	#7402	0.14	No	No	1 log	No	1 log	No
2%	#400	0.03	No	1 log	6 log	6 log	6 log	6 log
	#7402	0.07	No	No	6 log	1 log	6 log	6 log
4%	#400	0.47	6 log	6 log	6 log	6 log	6 log	6 log
	#7402	0.45	6 log	6 log	6 log	6 log	6 log	6 log
6%	#400	0.70	6 log	6 log	6 log	6 log	6 log	6 log
	#7402	0.70	6 log	6 log	6 log	6 log	6 log	6 log

#400 is 100% cotton plain woven fabric and #7402 is a 65/35 polyester/cotton plain woven fabric. Six log reduction means total kill.

Table IV illustrates the effects of chlorine concentrations on biocidal properties of the antibacterial fabrics finished using the protocol set forth in Example I. Every cycle of regeneration with different concentrations of chlorine will result in slight damages to the grafted heterocyclic rings. A concentration of 4% of monomethylol-5,5-dimethylhydantoin was selected as the finishing bath, and the take-up rate of the Anti-1 was 1.29%. The results obtained show some unexpected results for the #7402 fabric, which has more durable biocidal properties than cotton fabrics. Regeneration of the biocidal properties with lower chlorine concentration is preferred.

Table IV. Effects of Chlorine Concentration on Biocidal Properties (Bacterial Reduction Rates)

Cl%	Fabric	After five Washings		After ten Washings		After fifteen washings		After twenty washings	
		E. coli	S. aur.	E. coli	S. aur.	E. coli	S. aur.	E. coli	S. aur.
0.01	#400	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log
	#7409	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log
0.1	#400	6 log	6 log	6 log	6 log	6 log	6 log	1 log	0 log
	#7409	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log
0.25	#400	6 log	6 log	2 log	0 log	1 log	0 log	1 log	0 log
	#7409	6 log	6 log	6 log	6 log	6 log	6 log	1 log	1 log

#400 is 100% cotton and #7409 is a 65/35 polyester/cotton blend. Contact time = 60 min. Six log reduction means total kill of bacteria. Zero log reduction means some reduction of bacterial growth and extended contact causes further reduction. Washing tests were following AATCC-124 using machine washing warm (140°C) for 15 min. and 90 grams of AATCC detergent 124.

Example VI

This example illustrates the quantitative antibacterial study (AATCC Test Method 100) of Anti-2 finished fabrics.

Fabrics finished in accordance with the protocol set forth in Example II with Anti-2, *i.e.*, 1,3-dimethylol-5,5-dimethylhydantoin, were also tested with AATCC test method 100, which was briefly described in Example IV. In the tests, a diluted Clorox solution containing 0.01 % active chlorine was used to chlorinate the finished fabrics. The biocidal properties of Anti-2 finished fabrics are set forth in Table V.

Table V. Durable Antibacterial Properties of Anti-2 Finished Fabrics

Conc of Anti-2	Fabric	After five washes		After ten washes		After fifteen washes		After twenty washes		After twenty washes	
		E. coli	*S. aur.*	*E. coli*	*S. aur.*	*E. coli*	*S. aur.*	*E. coli*	*S. aur.*	*E. coli*	*S. aur.*
2%	#400	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log
	#7409	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log
6%	#400	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log
	#7409	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log
10%	#400	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log
	#7409	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log	6 log

#400 is 100% cotton and #7409 is a 65/35 polyester/cotton blend. Contact time=60 min. Six log reduction means total kill of bacteria. Zero log reduction means some reduction of bacterial growth and extended contact causes further reduction. Washing tests were following AATCC-124 using machine washing warm (140°C) for 15 min. and 90 grams of AATCC detergent 124.

Example VII

This example illustrates the durable press properties of Anti-2 finished fabrics.

Fabrics finished with Anti-2 in accordance with the protocol set forth in Example II also exhibit durable press properties, which is understandable because the structure of DMDMH is very similar to that of 1,3-dimethylol-4,5-dihydroxylethylene urea (DMDHEU). Durable press properties were tested according to AATCC Test Method 66. In the tests, six warp specimens and six filling specimens of #400 cotton fabrics having the size of 15x40 mm were conditioned in a conditioning room ($21 \pm 1°$ C and $65 \pm 2\%$ relative humidity) for over 24 hours. The wrinkle recovery angles of twelve samples which were creased with three warp and filling specimens on face side and three warp and filling specimens on back side were measured. Table VI shows the average wrinkle recovery angles of the finished fabrics after repeated washings. With higher concentration of the finishing agent, more functional agents are combined on the fabrics. Therefore, more cross-linking between cellulose chains is formed and better wrinkle resistant properties of the fabrics is expected.

Table VI. Wrinkle Recovery Angles of Anti-2 Finished #400 Pure Cotton Fabrics

Conc. of Anti-2	Average Wrinkle Recovery Angle (degree)						
	Before washing	After 5 washing	After 10 washing	After 15 washing	After 20 washing	After 25 washing	After 30 washing
0	87.0	/	/	/	/	/	/
2%	88.3	97.2	100.4	96.0	97.8	103.0	99.2
6%	115.4	111.8	108.4	111.2	111.0	111.2	109.8
10%	120.0	117.8	114.8	112.1	114.8	113.8	112.7

Washing conditions were same as that in Example III and Example V.

Example VIII

This example illustrates the effects of pH and dipping time on biocidal activity.

Based on the proposed reaction mechanism, the modification reaction, *i.e.*, the coupling reaction, prefers acidic conditions. As such, a lower pH is generally preferred during the finishing process. The reaction time also has an effect on the results of the chemical modification. The reaction time and pH values of finishing solutions were varied. Acidic conditions with lower pH values increased the pick-up rate of finishing agent by the finished fabrics, a finding which is consistent with the expected reaction mechanism. For instance, lowering the pH from 4.6 to 2.5 almost doubled the pick-up rates (Table VII). However, extended reaction times do not generally have real significant effects on the yields of the finishing fabrics.

Table VII. Biocidal Properties of Cotton Fabrics Processed Under Different pH's and Dipping Times

pH	Dipping Time (min)	Pick-up rate %	Biocidal result against *E.Coli* after 1st wash	after 5 or 8 washes
2.50	30	2.83	>5 mm	kill all
4.65	30	1.42	>2 mm	>3 mm
2.47	5	2.88	>1 mm	kill all
4.56	5	1.64	>2 mm	>3 mm

In addition, the finished fabrics were also tested in extensive washing tests. Generally, after 5-8 times of machine-washing according to AATCC Test Method 124, the fabrics were recharged with chlorine bleach and were tested against the bacteria. The disinfection distances of the samples still indicated that the fabrics finished under lower pH have strong bactericidal abilities.

Example IX

This example illustrates the breaking strength of the finished fabrics treated with Anti-1.

Table VIII indicates the breaking strength retention of the Anti-1 finished fabrics after extensive washes and regenerations of biocidal properties with different chlorine concentrations. The fabrics were finished in a solution with a concentration of 4% of monomethylol-5,5-dimethylhydantoin, and the take-up rate of the Anti-1 on the fabrics was 1.29%. Washing conditions were the same as in Table IV. Tensile strength of the fabrics were tested following American Society for Testing and Materials (ASTM) test method D1682. In the tests, a number of ravelled specimens with their long dimension parallel to filling of the fabrics was prepared in size of 25.4mm x 152.4mm. Then, breaking load of the fabrics was recorded in pound (lb).

Table VIII. Breaking Strength Retention of Some Anti-I Finished Fabrics

C1%	Breaking Strength, lb (% retention)							
	Fabric	Before	After treatment	After Bleach	After 5 washes + Bleach	After 10 washes + Bleach	After 15 washes + Bleach	After 20 washes + Bleach
0.01	#400	31.75	24.30 (77%)	23.43 (74%)	23.27 (73%)	20.14 (63%)	20.35 (64%)	19.46 (61%)
	#7509	30.71	32.27 (100%)	33.00 (100%)	32.41 (100%)	31.16 (100%)	31.80 (100%)	32.06 (100%)
0.1	#400	31.75	24.30 (77%)	22.75 (74%)	22.47 (74%)	19.63 (62%)	20.00 (63%)	19.45 (61%)
	#7409	30.71	32.27 (100%)	33.72 (100%)	32.75 (100%)	31.82 (100%)	31.80 (100%)	31.86 (100%)
0.25	#400	31.75	24.30 (77%)	22.30 (70%)	19.32 (61%)	19.25 (61%)	20.32 (64%)	18.04 (60%)
	#7409	30.71	32.27 (100%)	32.83 (100%)	33.34 (100%)	33.75 (100%)	32.38 (100%)	31.46 (100%)

It is to be understood that the above description is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should, therefore, be determined not with reference to the above description, but should instead be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. The disclosures of all articles and references, including patent applications and publications, are incorporated herein by reference for all purpose.

WHAT IS CLAIMED IS:

1. A composition for finishing fabric, said composition comprising:
a wetting agent; and
a heterocyclic *N*-halamine.

2. The composition of claim 1 wherein said heterocyclic *N*-halamine is a member selected from the group consisting of monomethylol-5,5-dimethylhydantoin (MDMH), 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH); monomethylolated and dimethylolated derivatives of 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid and 5,5-dimethylhydantoin; and monomethoxylated and dimethoxylated derivatives of monomethylolated and dimethylolated derivatives of 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid, 5,5-dimethylhydantoin 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid and 5,5-dimethylhydantoin.

3. The composition of claim 1 wherein said heterocyclic *N*-halamine is monomethylol-5,5-dimethylhydantoin.

4. The composition of claim 1 wherein said heterocyclic *N*-halamine is 1,3-dimethylol-5,5-dimethylhydantoin.

5. The composition of claim 1 wherein said wetting agent is a member selected from the group consisting of Triton X-100, SEQUAWET® and AMWET®.

6. The composition of claim 1 further comprising a catalyst.

7. The composition of claim 6 wherein said catalyst is a member selected from the group consisting of magnesium salts, zinc salts and ammonium salts.

8. The composition of claim 6 wherein said catalyst is a member selected from the group consisting of $MgCl_2$, $Mg(NO_3)_2$, $Zn(NO_3)_2$ and NH_4NO_3.

9. The composition of claim 1 wherein said composiiton has a pH of about 2 to about 6.

10. A process for preparing a microbiocidal cellulosic textile precusor, said process comprising:

(a) immersing a cellulosic textile in an aqueous treating solution which comprises a catalyst, a wetting agent and a heterocyclic *N*-halamine;

(b) removing the excess treating solution from said cellulosic textile;

(c) drying said cellulosic textile;

(d) curing said dried cellulosic textile;

(e) washing said cured cellulosic textile to remove excess reagents; and

(f) drying said cellulosic textile to remove water.

11. The process of claim 10 wherein said cellulosic textile is a cotton fabric.

12. The process of claim 10 wherein the cellulosic textile is paper.

13. The process of claim 10 wherein said heterocyclic *N*-halamine is a member selected from the group consisting of monomethylol-5,5-dimethylhydantoin (MDMH), 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH); monomethylolated and dimethylolated derivatives of 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid and 5,5-dimethylhydantoin; and monomethoxylated and dimethoxylated derivatives of monomethylolated and dimethylolated derivatives of 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid, 5,5-dimethylhydantoin 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid and 5,5-dimethylhydantoin.

14. The process of claim **10** wherein said heterocyclic *N*-halamine is monomethylol-5,5-dimethylhydantoin (MDMH).

15. The process of claim **10** wherein said heterocyclic *N*-halamine is 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH).

16. The process of claim **10** wherein said wetting agent is a member selected from the group consisting of Triton X-100, SEQUAWET® and AMWET wetting agents.

17. The process of claim **10** wherein said catalyst is a member selected from the group consisting of magnesium salts, zinc salts and ammonium salts.

18. The process of claim **10** wherein said catalyst is a member selected from the group consisting of $MgCl_2$, $Mg(NO_3)_2$, $Zn(NO_3)_2$ and NH_4NO_3.

19. A microbiocidal cellulosic textile precursor, said cellulosic textile precursor prepared by the process of claim **10.**

20. A process for rendering a cellulosic textile microbiocidal, said process comprising:

(a) washing a microbiocidal cellulosic textile precursor with a halogenated solution, said microbiocidal cellulosic textile precursor being prepared in accordance with claim **10**; and

(b) drying said treated microbiocidal cellulosic textile to remove water.

21. As a textile material, the microbicidal cellulosic textile treated by the process of claim **20.**

22. As a textile material, cotton fabric treated by the process of claim **20.**

23. A process for preparing a microbiocidal cellulosic/polyester textile precusor, said process comprising:

(a) immersing a cellulosic/polyester textile in an aqueous treating solution which comprises a catalyst, a wetting agent and a herterocyclic *N*-halamine;

(b) removing the excess treating solution from said cellulosic/polyester textile;

(c) drying said cellulosic/polyester textile;

(d) curing said dried cellulosic/polyester textile;

(e) washing said cured cellulosic/polyester textile to remove excess reagents; and

(f) drying said washed cellulosic/polyester textile to remove water.

24. The process of claim 23 wherein said cellulosic/polyester textile is a cotton/polyester fabric.

25. The process of claim 23 wherein said heterocyclic *N*-halamine is a member selected from the group consisting of monomethylol-5,5-dimethylhydantoin (MDMH), 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH); monomethylolated and dimethylolated derivatives of 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid and 5,5-dimethylhydantoin; and monomethoxylated and dimethoxylated derivatives of monomethylolated and dimethylolated derivatives of 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid, 5,5-dimethylhydantoin 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid and 5,5-dimethylhydantoin.

26. The process of claim 23 wherein said heterocyclic *N*-halamine is monomethylol-5,5-dimethylhydantoin (MDMH).

27. The process of claim 23 wherein said heterocyclic *N*-halamine is 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH).

28. A microbiocidal cellulosic/polyester textile precursor, said cellulosic/polyester textile precursor prepared by the process of claim 23.

29. A process for rendering a cellulosic/polyester textile microbiocidal, said process comprising:

(a) washing a microbiocidal cellulosic/polyester textile precursor with a halogenated solution, said microbiocidal cellulosic/polyester textile precursor being prepared in accordance with claim 23; and

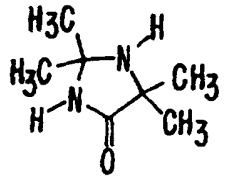
(b) drying said treated microbiocidal cellulosic/polyester textile to remove water.

30. As a textile material, the microbiocidal cellulosic/polyester textile treated by the process of claim 29.

31. As a textile material, cotton/polyester fabric treated by the process of claim 29.

32. A textile material having a cellulosic surface with a herterocyclic *N*-halamine covalently attached thereto.

33. The textile material of claim 32 wherein said heterocyclic *N*-halamine is a member selected from the group consisting of monomethylol-5,5-dimethylhydantoin (MDMH), 1,3-dimethylol-5,5-dimethylhydantoin (DMDMH); monomethylolated and dimethylolated derivatives of 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid and 5,5-dimethylhydantoin; and monomethoxylated and dimethoxylated derivatives of monomethylolated and dimethylolated derivatives of 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid, 5,5-dimethylhydantoin 2,2,5,5-tetramethyl-1,3-imidazolidin-4-one, 6,6-dimethyl-1,3,5-triazine-2,4-dione, 4,4,5,5-tetramethyl-1,3-imidazolidin-2-one, cyanuric acid and 5,5-dimethylhydantoin.



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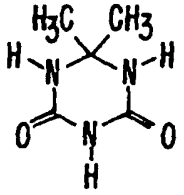

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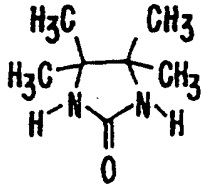

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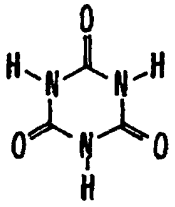
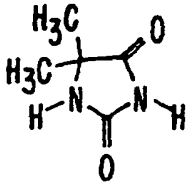
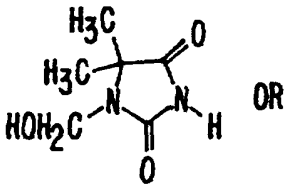


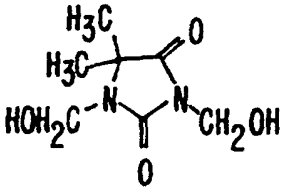
CYANURIC ACID



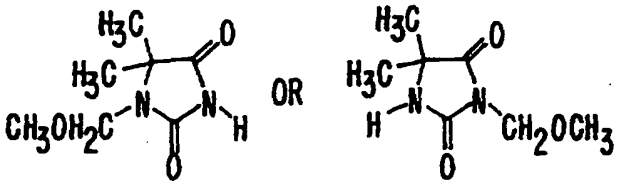
5,5-DIMETHYLHYDANTOIN



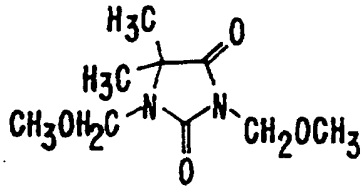
MONOMETHYLOL-5,5-DIMETHYLHYDANTOIN (MDMH)



1,3-DIMETHYLOL-5,5-DIMETHYLHYDANTOIN (DMDMH)



MONOMETHOXYMETHYL-5, 5-DIMETHYLHYDANTOIN



1,3-DIMETHOXYMETHYL-5,5-DIMETHYLHYDANTOIN

FIG. 1.

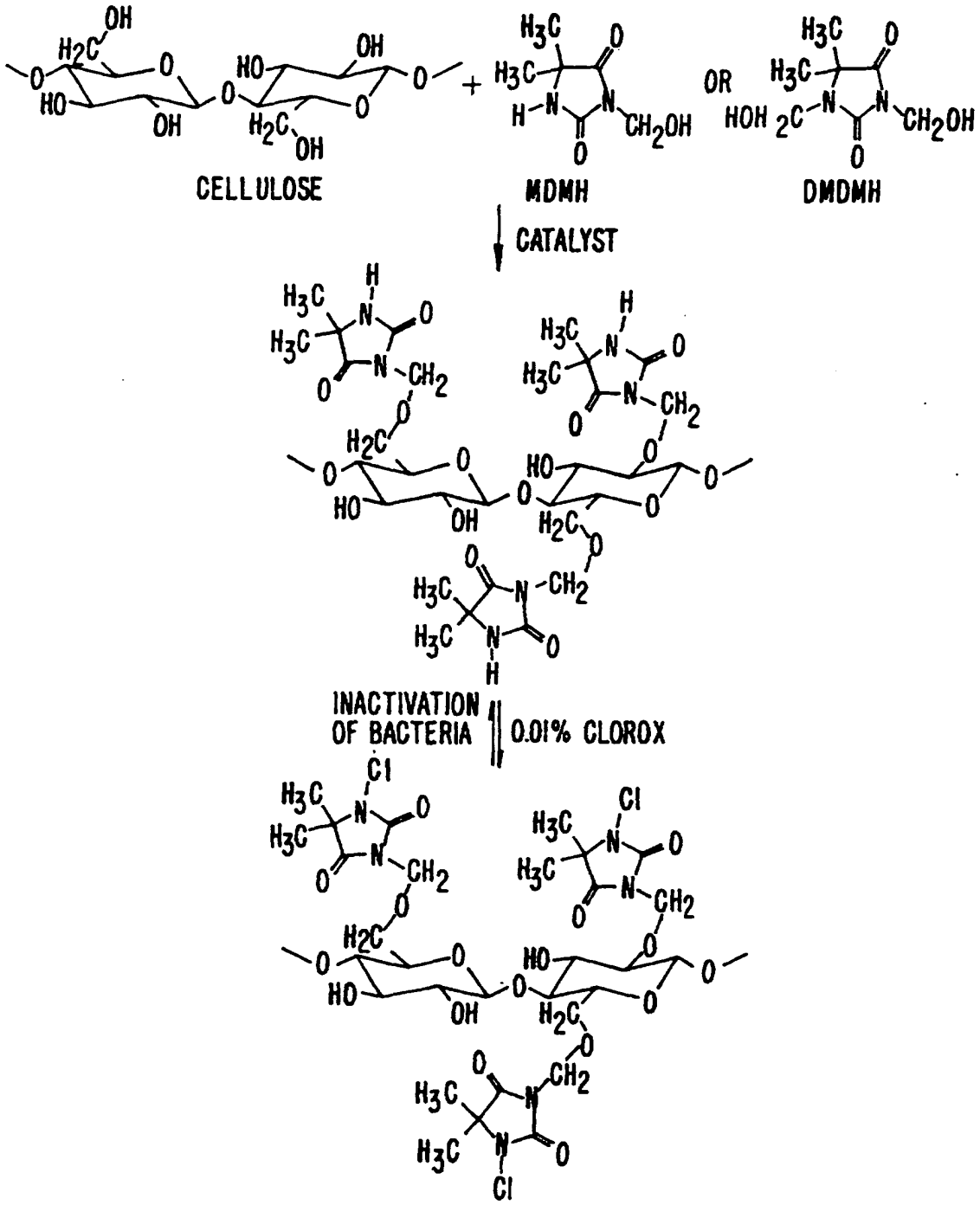


FIG. 2.

INTERNATIONAL SEARCH REPORT

International application N .
PCT/US97/16749

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A01N 33/00; D06M 13/35, 13/352, 13/355, 13/358, 13/364

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 8/181, 189, 190, 191, 115.57, 115.58, 115.59, 115.61; 252/8.84, 8.86, 8.91; 424/405

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2,950,553 A (HURWITZ) 30 August 1960, column 3, lines 24-50; and column 5, lines 1-46.	1, 6-12, 17-19, 23, 24, 28, 32 --- 2-5, 13-16, 20-22, 25-27, 29-31, 33
X --- Y	US 3,812,201 A (BEY) 21 May 1974, column 4, lines 12-25; and column 5, lines 48-75.	1, 5-9 --- 2-4, 10-33

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
08 DECEMBER 1997	14 JAN 1998

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	ALAN D. DIAMOND
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Form PCT/ISA/210 (second sheet)(July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/16749

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim N .
X ----- Y	GB 2,161,399 A (TURABI) 15 January 1986, page 1, lines 45-59.	1, 6, 8 ---------- 5, 9
X ----- Y	Chem. abstr., Vol. 78, No. 12, 26 March 1973 (Columbus, OH, USA), page 66, column 1, the abstract No. 73517u, BOGATYREVA, L.M. et al 'Wrinkleproof Finishing of Cotton Blended Fabrics.' Khlopchatobum. Prom. 1971, 31(2), 71-9 (Russ).	1, 6, 7, 9 ---------- 2-5, 8, 10-33
Y	US 3,445,279 A (ABRAHAMS ET AL) 20 May 1969, column 3, lines 27-57.	1-33
Y	US 3,565,824 A (PIERCE ET AL) 23 February 1971, column 3, lines 15-27; and column 4, lines 30-55.	1-33
Y	US 5,576,591 A (CUSANO ET AL) 27 April 1971, column 6, lines 1-59.	1-33
A	US 5,490,983 A (WORLEY ET AL) 13 February 1996.	1-33

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/16749

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

INTERNATI NAL SEARCH REPORT

International application No.
PCT/US97/16749

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

8/181, 189, 190, 191, 115.57, 115.58, 115.59, 115.61; 252/8.84, 8.86, 8.91; 424/405

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-9, drawn to a composition.
Group II, claim(s) 10-33, drawn to a process.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The technical feature which is common for the composition and process is the composition containing a wetting agent and a heterocyclic N-halamine. However, such a composition is not a special technical feature because it is known in the prior art. For example, Chemical Abstract No. 78:73517 discloses a composition containing LEUNA [CA Reg. No. 37218-01-2] surfactant which is a wetting agent, and Karbamol TsEM [CA Reg. No. 1852-21-7] which is a heterocyclic N-halamine.